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Signed

Dated 13 November 2003

GB0226715.1

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of:-

MICROMASS UK LIMITED
Incorporated in the United Kingdom
Atlas Park
Simonsway
MANCHESTER
M22 5PP
United Kingdom

ADP No. 07649676002

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Patents Act 1977
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Request for grant of a patent

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The Patent Office
Cardiff Road
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1. Your reference 85:79804

15 NOV 2002

2. Patent application number *(The Patent Office will fill in this part)* 0226715.1

18NOV02 E763940-1 D00027
P01/7700 0.00-0226715.1

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Micromass Limited
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United Kingdom

SECTION 30 (1) (PCT) APPLICATION FILED 02.06.03

Patents ADP number *(if you know it)* 08716102001

If the applicant is a corporate body, give country/state of incorporation: UK

4. Title of the invention: Mass Spectrometer

5. Name of your agent *(if you have one)*: Frank B. Dehn & Co.

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*:
179 Queen Victoria Street
London
EC4V 4EL

Patents ADP number *(if you know it)*: 166001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

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Continuation sheets of this form	
Description	8
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Priority documents	–
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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	–
Request for preliminary examination and search *(Patents Form 9/77)*	–
Request for substantive examination *(Patents Form 10/77)*	–
Any other documents *(please specify)*	–

11. I/We request the grant of a patent on the basis of this application.

Signature Date 15 November 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

P.M. Jeffrey
01273 244200

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Magnetic Sector Mass Spectrometer with Split Detector

Introduction

The magnetic sector is the oldest type of mass analyser. It is now only one of several different types of mass spectrometer manufactured commercially, but it remains the instrument of choice for a number of important applications, in particular in the areas of target compound trace analysis, accurate mass measurement, isotope ratio measurement and fundamental ion chemistry studies. This invention provides a means of improving the performance of a magnetic sector mass spectrometer when used for target compound trace analysis.

Magnetic Sector Mass Spectrometers – State of the Art

a) Principal of operation

Ions with mass (m) and charge (ze) accelerated through an electrical potential difference (V) will have velocity (v) and kinetic energy (ε) where:

$$\varepsilon = zeV = \tfrac{1}{2} m v^2 \qquad (1)$$

Ions with charge (ze) moving through a magnetic field (B) with velocity (v) are subject to the Lorentz force (F) orthogonal to the direction of the field and direction of travel. Consequently ions travel with a circular trajectory with radius (r_m) in which the centripetal force is provided by the Lorentz force:

$$F = Bzev = m (v^2 / r_m) \qquad (2)$$

Eliminating (v) from equations (1) and (2):

$$m/ze = B^2 r_m^2 / 2V \qquad (3)$$

In its simplest form the mass spectrometer transmits ions of a particular mass and charge from source to detector via a circular trajectory through a magnetic sector. Here the magnetic sector is a mass filter, and a mass spectrum can be recorded by scanning the magnetic field or accelerating voltage with serial detection of mass peaks. For some applications several detectors may simultaneously record several different ion masses each taking a different trajectory. Alternatively an array of detectors may be used to simultaneously record a portion of the mass spectrum.

b) Single focusing optics

An ion moving in a magnetic field is dispersed with respect to its momentum (p). The momentum of an ion is given by:

$$p = mv = (2m.\varepsilon)^{\frac{1}{2}} \qquad (4)$$

Therefore ions with the same kinetic energy (ε) are, in effect, dispersed with respect to their mass. In addition, the shape of the magnetic sector can be designed to have ion directional focusing properties. A magnetic sector of a particular shape and size will have a particular combination of ion dispersion and directional focusing characteristics.

An arrangement which combines an ion source with an ion beam width defining slit, a magnetic sector with convergent directional focusing characteristics and an ion 'collector' slit positioned at the image point of the source slit is defined as single focusing. The magnetic sector directional focusing

characteristics can be designed to a very high order, but its imaging properties will be limited by any spread in ion energy. An example of a single focusing arrangement is shown in figure 1.

c) Mass dispersion and resolution

The mass dispersion coefficient (D_m) of a single focusing magnetic sector is proportional to the radius of curvature (r_m) of the ion beam trajectory in the magnetic field. The spatial separation (y) of two ions with mean mass (m) and mass difference (Δm) is related to the mass dispersion coefficient by:

$$y = D_m.\Delta m/m \qquad (5)$$

The ion beam width (w_b) at the image position is related to the ion beam width defined by the source slit (w_s), the image lateral magnification (M) and the sum of the imaging aberration coefficients ($\Sigma\alpha$) by:

$$w_b = M.w_s + \Sigma\alpha \qquad (6)$$

The mass resolving power ($m/\Delta m$) for a 'collector' slit width (w_c) is given by:

$$m/\Delta m = D_m / (w_b + w_c) = D_m / (M.w_s + w_c + \Sigma\alpha) \qquad (7)$$

Thus, the mass dispersion coefficient and the slit widths are the most significant parameters in setting the resolution. However, ultimate resolution is limited by the imaging aberrations.

d) Double focusing optics and high resolution

It has been pointed out that the magnetic sector will disperse ions with respect to their momentum, and hence with respect to their mass if they are mono-energetic. However, ions will normally have a spread in kinetic energy, depending on the nature of the ion source, and this will broaden the image width. This usually becomes the limiting factor to achieving high resolution

Momentum dispersion may be considered a combination of mass dispersion and energy dispersion. An electric sector will only disperse ions with respect to their energy, and so if an electric sector is combined with a magnetic sector the overall energy dispersion will be modified. A combination of magnetic sector and electric sector which is directional focusing and in which the overall energy dispersion is zero is said to be double focusing. Such a combination need not suffer the same image broadening due to spread in ion kinetic energy, and can achieve much higher resolution.

If the first sector has energy dispersion D_{e1}, and the second sector has energy dispersion D_{e2}, and image magnification of the second sector is M_2, then the overall energy dispersion (D_e) is

$$D_e = M_2.D_{e1} + D_{e2} \qquad (8)$$

The electric sector may precede or follow the magnetic sector, or be divided into two smaller electric sectors positioned before and after the magnetic sector. Provided the overall energy dispersion (D_e) is zero the arrangement is double focusing. An example of such an arrangement is shown in figure 2.

The combination of magnetic and electric sectors to form a double focusing arrangement includes sufficient degrees of freedom in the choice of design to allow higher order focusing to be achieved. Double focusing instruments, in which all second order directional and energy focussing terms are near zero, have been constructed and achieved resolving powers in excess of 150,000 by the 10% valley definition (based on peak width at 5% height). This capacity for high resolution enables double

focusing magnetic sector mass spectrometers to be used for accurate mass measurement, and for highly specific target compound trace analysis by the technique known as "high resolution selective ion recording" (HR-SIR).

e) High resolution selective ion recording (HR-SIR)

A double focusing magnetic sector mass spectrometer can be used to select and record the response from target compounds at high resolution and with a high sensitivity. The high resolution enables chemical background masses to be eliminated and consequently allow a lower detection level to be achieved. Selected ion recording provides a much better duty cycle, and therefore sensitivity, than scanning.

The detection and quantification of polychlorinated dibenzo-p-dioxins, and in particular the 2,3,7,8-tetrachlorinated dibenzo-p-dioxin, is a major application for double focusing magnetic sector mass spectrometers. Despite extensive clean-up procedures, samples still contain compounds such as polychlorinated biphenyls and benzylphenylethers, which have the same nominal masses as the compounds of interest. The sample is 'spiked' with a known amount of the ^{13}C isotope labelled form of 2,3,7,8-TCDD, introduced via gas chromatography and recorded by 'high resolution' mass spectrometry. The measurement is quantified by comparison of the native dioxin response to that from the ^{13}C labelled form, and verified by confirmation of the ratio of the major isotopes of both the native and the ^{13}C labelled dioxins. At 10,000 resolving power (10% valley definition) the detection level for 2,3,7,8-TCDD is about 1 femto-gram, or 3 atto-mole. Figure 3 shows an example of such a measurement.

f) Single and Parallel Detection

A magnetic sector mass spectrometer with a single detector may be used to record a mass spectrum by scanning and sequentially detecting mass peaks. The duty cycle for recording each mass in the spectrum is generally poor, and the higher the resolution or the wider the mass range the poorer the duty cycle. Unlike the quadrupole type of mass filter, a magnetic sector may be designed to record the signal from several different masses simultaneously. This is referred to as parallel detection, and takes two common forms:

(i) Multiple detectors

Multiple detectors provide a means of accurately recording the relative abundance of two or more different masses since measurement of the ratio of these peak intensities is not susceptible to fluctuations or drift in the ionisation source, or to rapidly changing sample concentration such as encountered in chromatography. Magnetic sector mass spectrometers incorporating multiple collector slits and corresponding discrete detectors are used to make the most accurate isotope ratio determinations. The different detectors are required to record different masses, and only at a low resolution, typically 200 ~ 300 (10% valley definition).

(ii) Array detectors

An array detector allows simultaneous acquisition over a range of masses thereby improving the duty cycle when used to record a spectrum. Array detectors employing high-density arrays of discrete charge sensitive detectors or 'single ion' position sensitive detectors are very sensitive, although are usually limited in size. Such detectors are normally positioned along the focal plane of the mass spectrometer and therefore replace the collector slit normally present when a detector is used. Hence, each detector in the array substitute for the collector slit, and it is these that determine the resolution. The detector is required to record several masses, and in practice can only operate at up to medium resolution, typically up to 2000 (10% valley definition). This is too low a resolution for the analysis of polychlorinated dibenzo-p-dioxins.

Limitation of the State of the Art

The high resolution selected ion recording measurement, as described for the detection of traces of 2,3,7,8-tetrachlorinated dibenzo-p-dioxin, entails repetitive rapid switching to at least four different masses at high resolution and recording the signal response for all four masses. This is commonly carried out at a mass resolution of 10,000 (10% valley definition) to ensure other isobaric components eluting from the GC column are separated out. In some instances it is necessary to operate at even higher resolution, for example at 20,000 resolution (10% valley definition). In practice an addition material is continuously infused into the ion source of the mass spectrometer such that an additional mass peak that is close in mass to that of the trace compound is continuously present. This is known as the reference peak. This mass is included in the switching sequence so that any drift in the mass scale can be monitored and corrected for. This is achieved by scanning across the reference peak to determine any shift in the peak centre. Otherwise the switching to the peak top of each of the four masses of interest could not be certain. It has now become common practice to switch to the reference peak a second time in each sequence to verify that the switching operation is working correctly and accurately.

This procedure ensures accurate switching at 10,000 resolution. However, it does not ensure that all ions detected are ions of the target compound of interest. Interference ions may be detected which are due to contamination materials in the source or reference material, or other eluting components from the GC, with very similar masses. These may be detected because they are not fully separated at 10,000 resolution, or because they have become scattered through a collision with a residual gas molecule. The main indication of a major interference is a distortion of the isotope ratio, and this is part of the standard verification procedure. Even when interference ions are present and recognised by their distorted isotopic ratio their presence contributes a background that may obscure the detection of the trace compound of interest. Simply switching from peak top to peak top does not provide a means in itself to verify detected ions are the ions of interest, or a means of discarding ions when they are not ions of the compound of interest.

The New Invention

The new invention described here is the substitution of a single detector by two separate detectors whilst still retaining a single collector slit. Each ion transmitted through the single collector slit is divided according to the position and direction of each ion onto one of the two detectors. An ion beam uniformly distributed across the collector slit, or distributed symmetrically about the centre of the collector slit, is divided substantially equally such that substantially half of the ion beam would arrive on each of the two detectors. Hence an ion beam that is not uniformly distributed across the collector slit, or is not distributed symmetrical about the centre of the collector slit, is distributed unequally on to the two detectors. Hence, by observing the relative signal on the two detectors it is possible to determine whether or not the ion beam is uniformly distributed across the collector slit or distributed symmetrical about the centre of the collector slit. This in turn provides a means of determining whether or not the ions detected are ions of interest, or that the ions detected are not ions of interest and may be discarded.

The preferred means for separating the ion beam consists of a finely edged blade parallel to the length of the collector slit. A high voltage is applied to the blade such that ions are repelled away from the blade. The centre of the blade is aligned with the centre of the collector slit such that ions in the centre of the beam, travelling in a central direction, are directed towards the centre of the blade. All other ions are deflected to one side or the other of the blade. The two detectors each detect ions that are deflected to one side or the other of the blade.

In a preferred embodiment, a lens is positioned after the collector slit and before the split detector. This is to refocus the image of the collector slit at the position of the split detector. Preferably the refocused image is magnified. This is to increase the spatial distribution of ions passing through the collector slit and arriving at the detector. Figure 4 shows a diagram of such an arrangement.

In the preferred embodiment the ions are directed towards the fine blade held at a high retarding potential, and peel off to one side or the other according to which side of the dead centre each ion is positioned. Figure 5 shows an example of such a split detector design. The ions enter through a screening tube and into a space in which they confront the fine blade. The retarding fields cause the ions to peel off and reflect back to one of the two detectors either side of the screening tube. In this example the two detectors are micro-channel plates, with anodes positioned behind the micro-channel plates. The anode receives a pulse of electrons for each ion arriving, and these electron bursts may be counted, or integrated and measured using an analogue-to-digital converter. The ion detectors could also be discrete dynode electron multipliers or continuous dynode channeltrons.

In another embodiment the ions are accelerated towards a conversion dynode, and the secondary electrons are detected using a micro-channel plate. Figure 6 shows an example of such an arrangement. The advantage of using a conversion dynode is that it can increase ion detection to near 100%. This is because a micro-channel plate typically has an open area ratio of 60 ~ 70%, and therefore it's ion detection efficiency will only be in the region of 60~70%. A conversion dynode will have 100% ion detection efficiency, and typically will yield between 2 and 6 electrons per ion. The probability that the micro-channel plate will detect at least one of these electrons is near 100%. An alternative arrangement is to accelerate the ions from the conversion dynode onto a scintillator or phosphor, and to detect the emitted light with a photo-multiplier tube (PMT) or photosensitive solid state detector.

In another embodiment there are positioned two detectors on each side of the blade, making a total of four detectors. In this arrangement the ion beam defected to one side of the central blade is further subdivided on to the two detectors according to their position and direction. Similarly the ion beam deflected to the other side of the central blade is subdivided on to the other two detectors. Figure 7 shows an example of such an arrangement. Such an arrangement would allow the determination of the asymmetry of the ion beam in greater detail. In another embodiment the number of detectors is a higher multiple of two.

In another embodiment a conventional detector may also be included in the arrangement. Figure 8 shows an example of such an arrangement. In this example the additional detector includes a conversion dynode, a focusing ring, a phosphor and a photo-multiplier. When the voltages on this detector are switched off the ions travel directly to the split detector without interruption. When the voltages on this additional detector are switched on the ions are deflected on to the conversion dynode and secondary electrons are accelerated and focused on to the phosphor. The additional detector can be used for recording ions in the conventional way.

Advantage of the New Invention

When the ion beam of a particular mass is scanned across the collector slit of a magnetic sector mass spectrometer the resulting signal profile is commonly called the peak profile. The peak profile will vary according to the relative width of the ion beam (w_b) and that of the collector slit (w_s). It will also vary according to the ion intensity profile of the ion beam. The high resolution selected ion recording measurement, as described for the detection of traces of 2,3,7,8-tetrachlorinated dibenzo-p-dioxin, is commonly carried out at a mass resolution of 10,000 (10% valley defn). A mass peak that has a width of 100 parts per million (ppm) of the mass when measured at 5% of it's maximum intensity, has a mass resolution of 10,000 (10% valley definition). A mass peak that is 100 ppm wide usually has maximum transmission when the collector slit width (w_s) is just equal to that of the ion beam width

(w_b); that is, when the collector slit and ion beam each have a width of 50 ppm. Under these conditions the source slit width (w_s) is as large as it can be for the collector slit to just transmit the total beam arriving at the collector slit, and for the peak width to be 100 ppm. Figure 9 shows an example of an ion beam and collector slit that are each 50 ppm wide and the resulting peak profile which is 100 ppm wide. The ion beam profile can vary according to a large number of parameters in the design of the mass spectrometer, although a profile that follows a cosine distribution is quite typical. The figure shows an ion beam profile with a cosine distribution, and when the ion beam width (w_b) is equal to the collector slit width (w_c) the resulting peak profile is that of a cosine squared distribution.

In the high resolution selected ion recording experiment the ion beam is switched to the central position, where just 100% of the ion beam is transmitted through the collector. This measurement does not allow any knowledge of the peak profile to be gained. The peak profile is only assumed to be as illustrated in figure 9. If the peak profile is not as expected, because the ions do not have precisely the right mass, or because they are randomly scattered ions from a nearby mass, this will not be known and the ions will still be recorded.

If instead the ion beam that is transmitted through the collector slit is detected on two detectors as described above, then the situation is quite difference. Figure 10 shows an example of an ion beam and collector slit that are each 50 ppm wide and the transmitted ions are detected using such a dual detector. The resulting peak profiles recorded on each detector are each 75 ppm wide and displaced by 25 ppm with respect to each other. If the two peak profiles were summed the resulting peak profile would be 100 ppm wide, and would be substantially the same as that recorded on a conventional single detector.

With such a dual detector system, in the high resolution selected ion recording experiment where the ion beam is switched to the central position, the ion signal recorded on each of the two detectors is the same, provided the ion beam is symmetrically disposed about the centre of the collector slit. Now, if the peak profile is not as expected, because the ions do not have precisely the right mass, or because they are randomly scattered ions from a nearby mass, the ion signal on the two detectors will not be equal. Hence it would now be possible to conclude that ions of the wrong mass are being detected and may be discarded. Equally, if the peak profile is as expected the ion signal on the two detectors will be substantially equal and it would now be possible to conclude that ions of the correct mass are being detected.

It will be seen from figure 10 each detector is not detecting the maximum number of ions that it would detect if the ion beam were shifted by 12.5 ppm. In other words, the ion beam is not positioned at the peak top for either detector, even though it is at the peak top for the sum of the detectors. This means a small shift in the ion beam will cause the signal on one detector to increase and that on the other to decrease. Hence, the arrangement is very sensitive to small shifts in the position of the ion beam.

The effect of a small shift in the ion beam is illustrated in table 1. In this example it is assumed that the resolution is 10,000 and that a total of only 20 ions have been transmitted through the collector slit and detected. The following explains the derivation of the numbers in each column of table 1:

1) Column 1 tabulates a series of shifts in the peak away from the centre in ppm.

2) Column 2 tabulates the number of ions that would be detected on the first detector for the corresponding shift.

3) Column 3 tabulates the number of ions that would be detected on the second detector for the corresponding shift

4) Column 4 tabulates the total number of ions detected, and is the sum of columns 2 and 3.

5) Column 5 tabulates the number of ions that would have been expected to have been detected on each detector had the peak been positioned in the centre, given the total count reported in column 4. In other words, column 5 simply reports half the total number of ions reported in column 4 for each peak shift.

6) Column 6 tabulates one standard deviation for the expected ion count for each detector reported in column 5.

7) Column 7 tabulates the difference between the actual ion count for the first detector, reported in column 2, and the ion count that would have been expected, as reported in column 5, expressed in terms of the number of standard deviations of the expected ion count tabulated in column 6.

8) Column 8 similarly tabulates the difference, in terms of standard deviations, between the actual ion count for the second detector, reported in column 3, and the expected count, reported in column 5.

9) Column 9 tabulates the percentage probability for the difference in ion count of the expected average being equal to or less than the actual difference in count reported for the first detector in column 7, assuming a natural or Gaussian distribution.

10) Likewise, column 10 tabulates the same percentage probability for the difference in count rate reported for the second detector in column 8.

11) Column 11 tabulates the percentage probability that the difference in count rates from the expected average, for both the first and second detectors, are greater than that to be expected assuming a natural or Gaussian distribution. In other words, column 12 reports the percentage probability of observing the two ion counts recorded on the first and second detectors for a peak with a total ion count equal to the sum of the two separate ion counts and positioned centrally.

It will be seen from table 1 that the ion counts on the two detectors from a peak of only 20 ions, shifted by 5 ppm, are such that the probability that the observed ion counts could be observed if the peak was positioned centrally is as high as 13%. However, the ion counts on the two detectors from a peak of only 20 ions shifted by 10 ppm are such that the probability that the observed ion counts could be observed if the peak was positioned centrally is now only 1%. Furthermore, the ion counts on the two detectors from a peak of only 20 ions, shifted by 15 ppm, are such that the probability that the observed ion counts could be observed if the peak was positioned centrally is now only 0.1%.

In this example, the benefit of the split detector is such that for the measurement of a peak of just 20 ions it could be ascertained with a 99% confidence that the peak is not an interfering peak displaced by only 10 ppm. Alternatively it could be ascertained with a 99.9% confidence that the peak is not an interfering peak displaced by only 15 ppm. Using a conventional single detector it would have been necessary to operate with a peak width at 5% height of only 20 ppm to achieve the same specificity. This corresponds to a resolution of 50,000 (10% valley definition). Hence, in this example, the split detector provides a five-fold increase in specificity. Alternatively, the split detector provides the same specificity at between 5 and 25 times more sensitivity since this is the likely loss in sensitivity to result from increasing the resolution of the mass spectrometer from 10,000 to 50,000.

Table 2 shows another example. Here the resolution has been reduced to 2000, and as a consequence it has been assumed the transmission has been increased by a factor of five so that the number of ions detected has increased to 100. It will be seen from table 2 that the ion counts on the two detectors from a peak shifted by 20 ppm are such that the probability that the observed ion counts could be observed if the peak was positioned centrally is only 1%.

In this example, the benefit of the split detector is such that for the measurement of a peak of 100 ions at 2000 resolution it could be ascertained with a 99% confidence that the peak is not an interfering peak displaced by only 20 ppm. Using a conventional single detector it would have been necessary to

operate with a peak width at 5% height of only 40 ppm to achieve the same specificity. This corresponds to a resolution of 25,000 (10% valley definition). Hence, in this example, the split detector provides both increases in sensitivity and specificity compared to that achieved with a single detector operating at 10,000 resolution.

The calculations here assume the mechanical arrangement of the split detector is perfect. In practice the tolerances on the positioning and alignment of the split detector will restrict the gain in performance over that of a single detector.

Hence, it will be seen that the split detector can improve the specificity of the analysis without loss in sensitivity, or can allow an improved sensitivity without loss in specificity, or allow both improved sensitivity and specificity. Furthermore, it is expected than random scattered ions that constitute background noise can be at least partially eliminated.

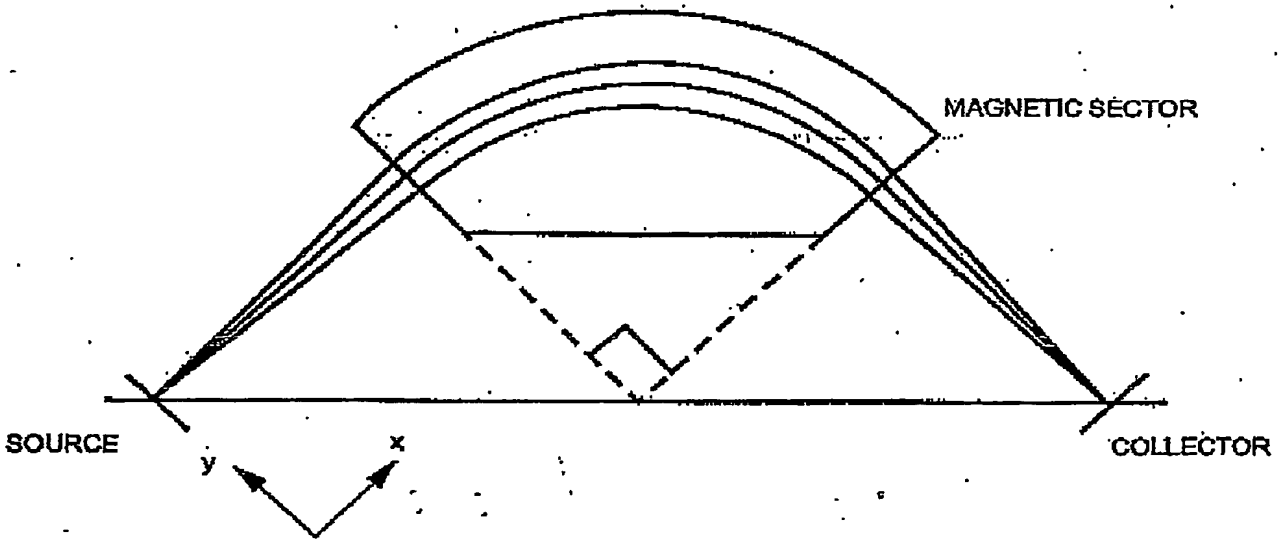

Figure 1

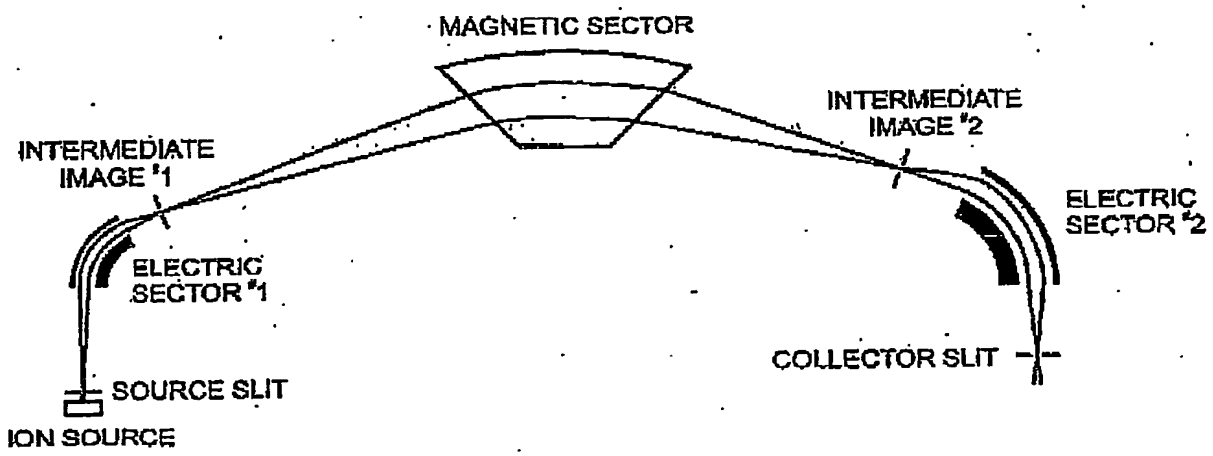
MAGNETIC SECTOR
INTERMEDIATE IMAGE #1
INTERMEDIATE IMAGE #2
ELECTRIC SECTOR #1
ELECTRIC SECTOR #2
SOURCE SLIT
ION SOURCE
COLLECTOR SLIT

Figure 2

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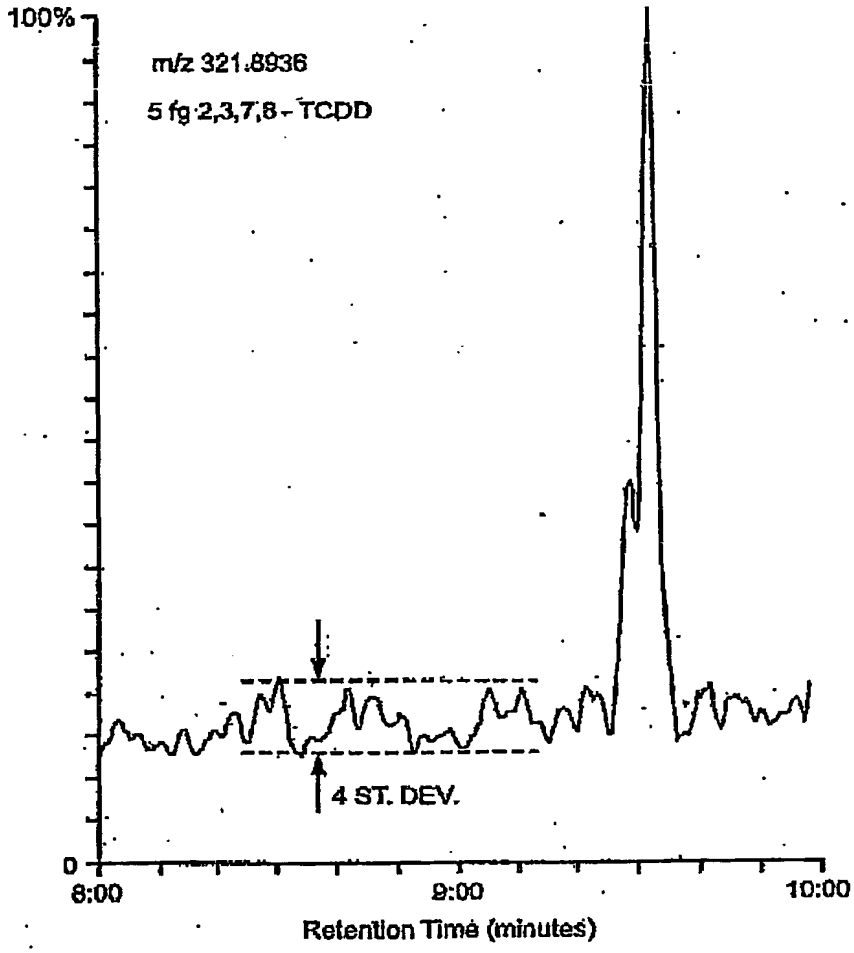
100%
m/z 321.8936
5 fg 2,3,7,8 - TCDD
4 ST. DEV.
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Retention Time (minutes)

Figure 3

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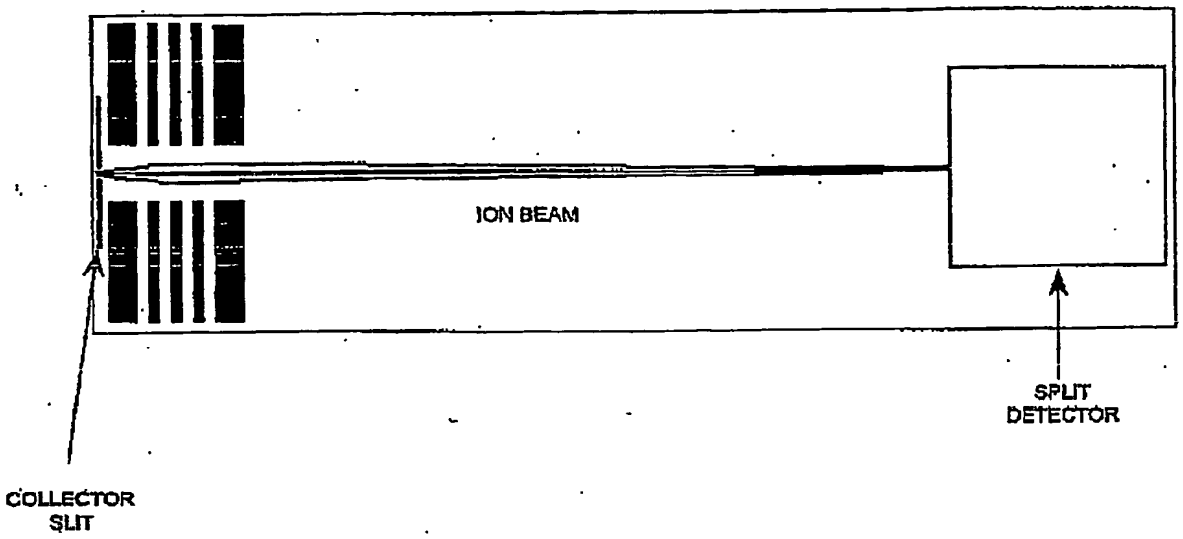

Figure 4

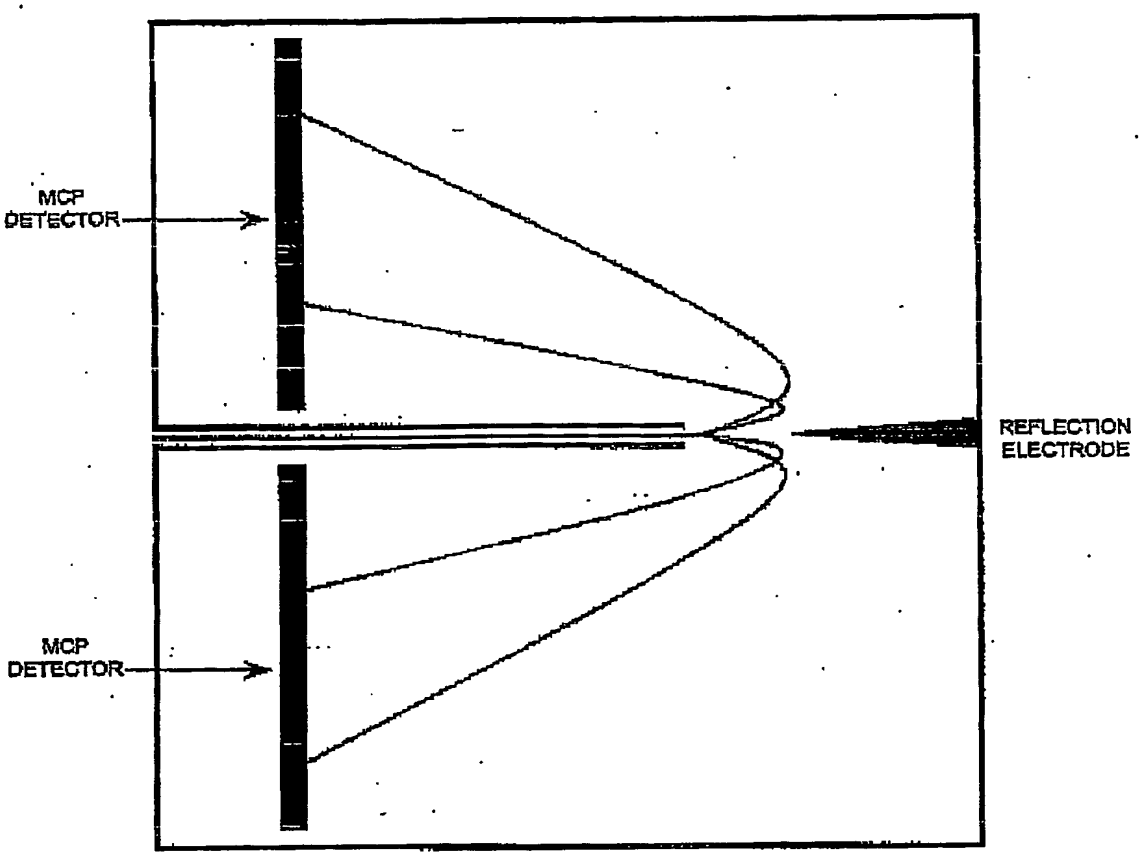

Figure 5

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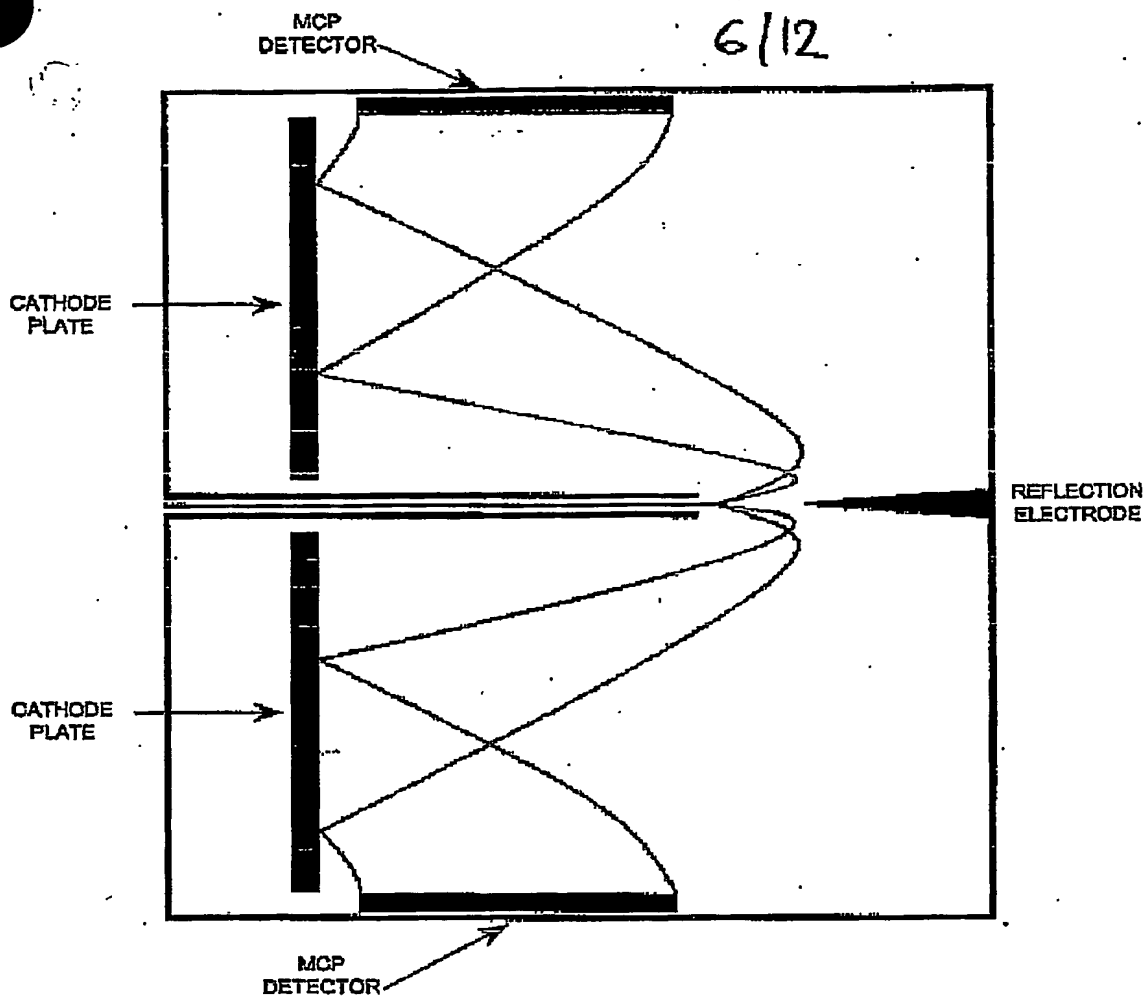
MCP
DETECTOR
CATHODE
PLATE
REFLECTION
ELECTRODE
CATHODE
PLATE
MCP
DETECTOR

Figure 6

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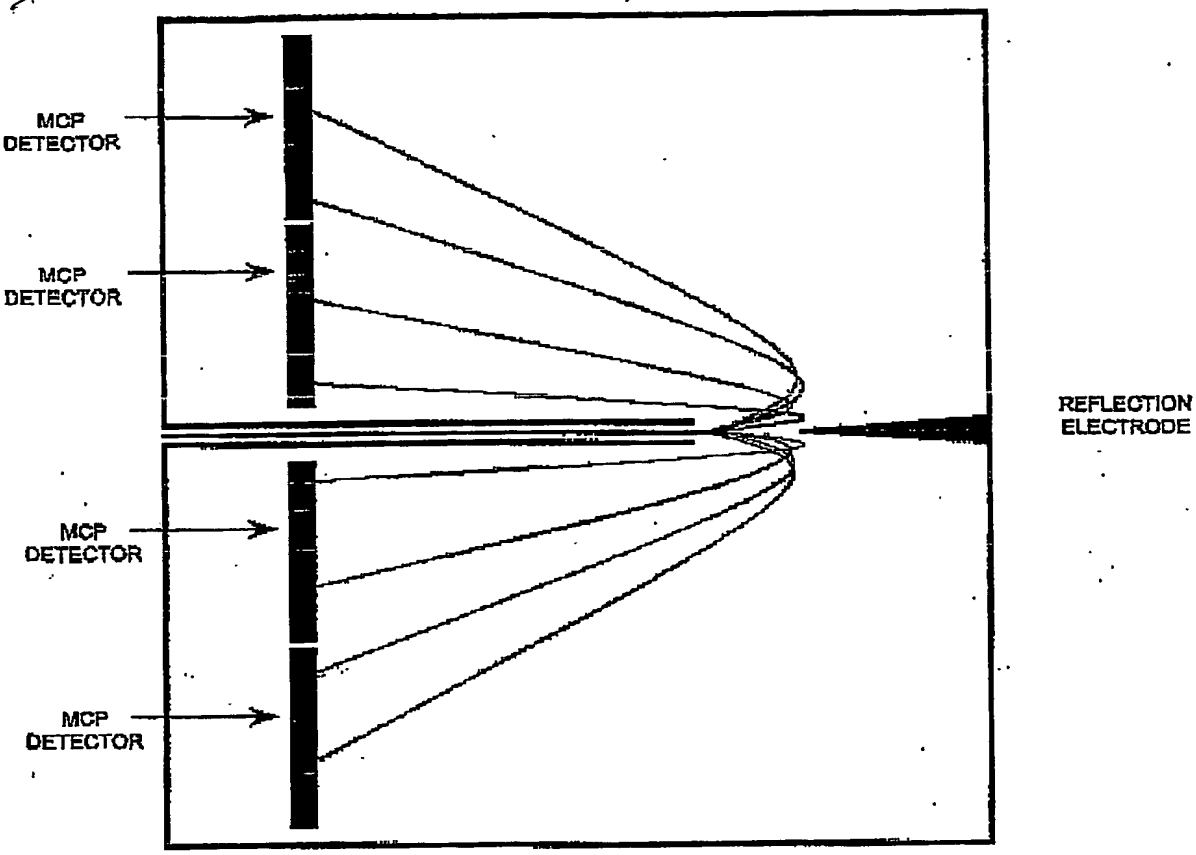
MCP
DETECTOR
MCP
DETECTOR
MCP
DETECTOR
MCP
DETECTOR
REFLECTION
ELECTRODE

Figure 7

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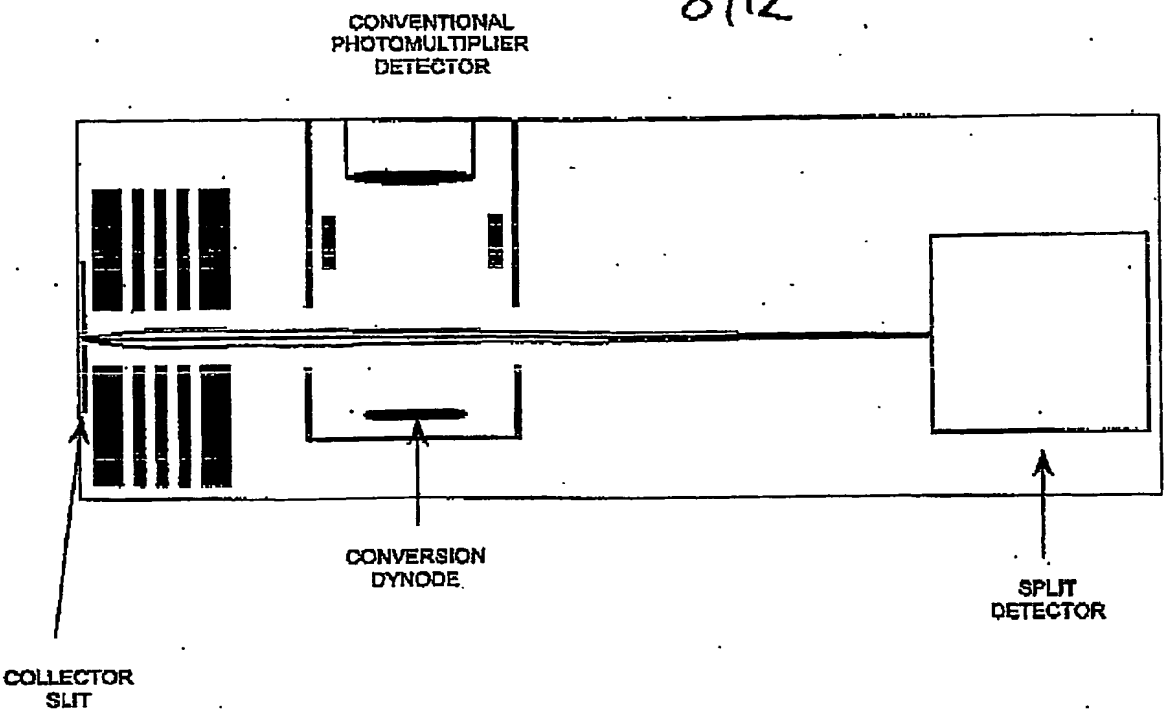
CONVENTIONAL
PHOTOMULTIPLIER
DETECTOR
CONVERSION
DYNODE
SPLIT
DETECTOR
COLLECTOR
SLIT

Figure 8

Single Detector

Beam width (w_b) = 50 ppm Collector slit width (w_s) = 50 ppm Peak width = 100 ppm

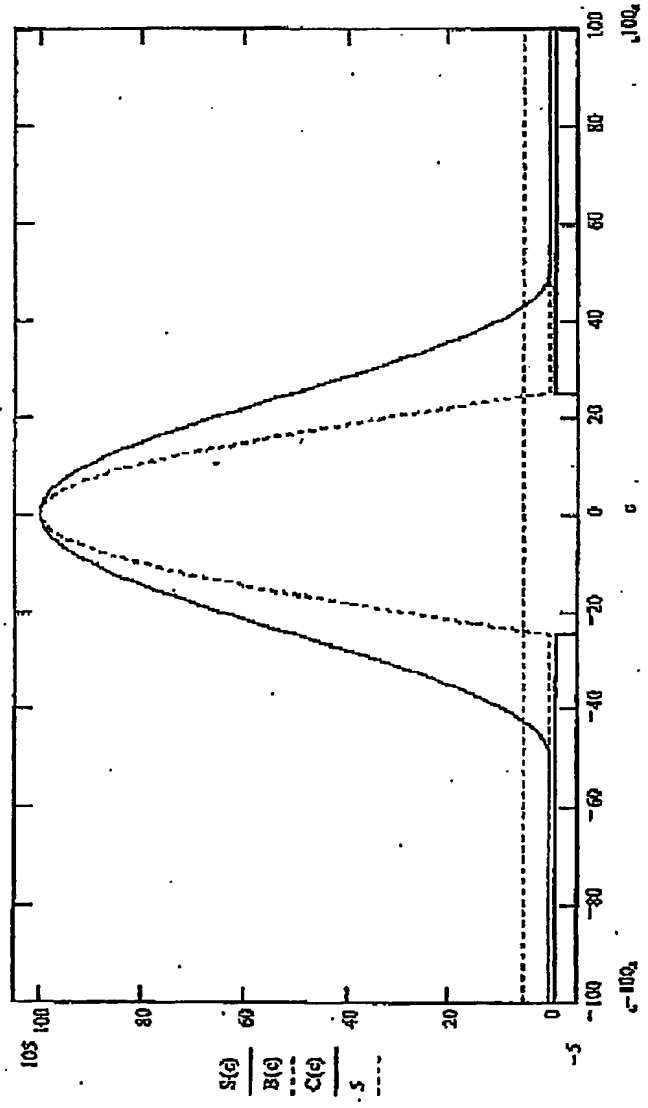

Figure 9

Dual Detector

Beam width (w_b) = 50 ppm Collector slit width (w_c) = 50 ppm Peak width = 100 ppm

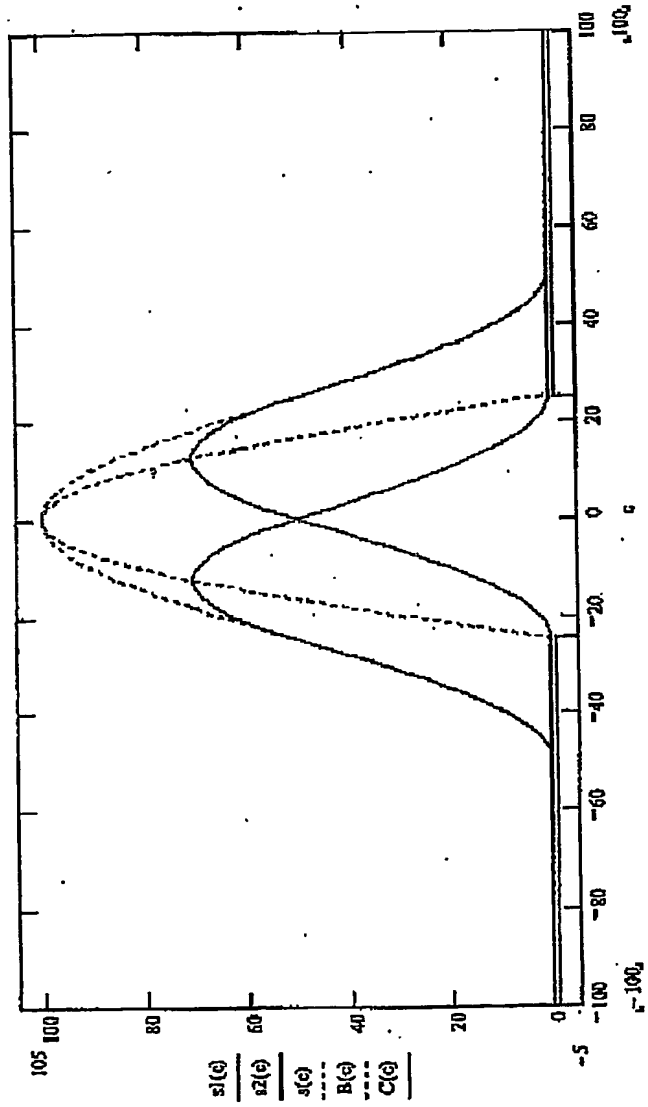

Figure 10

TABLE 1

Beam width (wb) = 50 ppm Collector slit width (wc) = 50 ppm Peak width = 100 ppm

Peak Shift (ppm) i =	Count on 1st detector s1(i) =	Count on 2nd detector s2(i) =	Total count s(i) =	Average count per detector sa(i) =	Std dev (σa) for average σa(i) =	Difference D1 in units of (σa) D1(i) =	Difference D2 in units of (σa) D2(i) =	P1 (%) P1(i) =	P2 (%) P2(i) =	P (%) Pr(i) =
-25	0	10	10	5	2.24	2.24	2.24	97.47	97.47	0.064
-20	0.5	12.6	13.1	6.55	2.56	2.37	2.37	98.21	98.21	0.032
-15	1.9	14	15.9	7.94	2.82	2.14	2.14	98.76	96.76	0.105
-10	4.1	14	18.1	9.05	3.01	1.64	1.64	89.83	89.83	1.033
-5	6.9	12.6	19.5	9.76	3.12	0.91	0.91	63.77	63.77	13.125
0	10	10	20	10	3.16	0	0	0	0	100
5	12.6	6.9	19.5	9.76	3.12	0.91	0.91	63.77	63.77	13.125
10	14	4.1	18.1	9.05	3.01	1.64	1.64	89.83	89.83	1.033
15	14	1.9	15.9	7.94	2.82	2.14	2.14	98.76	98.76	0.105
20	12.6	0.5	13.1	6.55	2.56	2.37	2.37	98.21	98.21	0.032
25	10	0	10	5	2.24	2.24	2.24	97.47	97.47	0.064

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TABLE 2

Beam width (wb) = 250 ppm Collector slit width (wc) = 250 ppm Peak width = 500 ppm

Peak Shift (ppm)	Count on 1st detector	Count on 2nd detector	Total count	Average count per detector	Std dev (σa) for average	Difference D1 in units of (σa)	Difference D2 in units of (σa)	P1 (%)	P2 (%)	P (%)
i =	s1(i) =	s2(i) =	s(i) =	sa(i) =	σa(i) =	D1(i) =	D2(i) =	P1(i) =	P2(i) =	P(i) =
-45	23.2	69	92.2	46.11	6.79	3.37	3.37	99.93	99.93	0
-40	25.9	67.9	93.8	46.91	6.85	3.07	3.07	99.78	99.78	0
-35	28.7	66.5	95.2	47.62	6.9	2.74	2.74	99.39	99.39	0
-30	31.6	64.9	96.5	48.24	6.95	2.4	2.4	98.35	98.35	0.027
-25	34.5	63	97.6	48.78	6.98	2.04	2.04	95.84	95.84	0.173
-20	37.6	60.9	98.4	49.21	7.02	1.66	1.66	90.32	90.32	0.937
-15	40.6	58.5	99.1	49.56	7.04	1.27	1.27	79.52	79.52	4.194
-10	43.7	55.9	99.6	49.8	7.06	0.86	0.86	61.02	61.02	15.191
-5	46.9	53	99.9	49.95	7.07	0.44	0.44	33.81	33.81	43.817
0	50	50	100	50	7.07	0	0	0	0	100
5	53	46.9	99.9	49.95	7.07	0.44	0.44	33.81	33.81	43.817
10	55.9	43.7	99.6	49.8	7.06	0.86	0.86	61.02	61.02	15.191
15	58.5	40.6	99.1	49.56	7.04	1.27	1.27	79.52	79.52	4.194
20	60.9	37.6	98.4	49.21	7.02	1.66	1.66	90.32	90.32	0.937
25	63	34.5	97.6	48.78	6.98	2.04	2.04	95.84	95.84	0.173
30	64.9	31.6	96.5	48.24	6.95	2.4	2.4	98.35	98.35	0.027
35	66.5	28.7	95.2	47.62	6.9	2.74	2.74	99.39	99.39	0
40	67.9	25.9	93.8	46.91	6.85	3.07	3.07	99.78	99.78	0
45	69	23.2	92.2	46.11	6.79	3.37	3.37	99.93	99.93	0

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